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(71)Applicant : NIPPON PAINT CO LTD

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(72)Inventor : SHIRAKAWA SHINSUKE
YAMADA MITSUO

(54) CATIONIC ELECTRODEPOSITION COATING COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cationic electrodeposition coating composition which has been improved in throwing power, prevention of pinholes due to a hydrogen gas, and prevention of cissing without detriment to dispersion stability in an aqueous medium.

SOLUTION: This coating composition contains an emulsion which is prepared by dispersing a binder component comprising an amine-modified epoxy resin and a blocked polyisocyanate curative in an aqueous medium containing a combination of an organic acid and a metal salt of an organic acid as a neutralizing agent. The total amount of the organic acid (including that present as the metal salt) contained is 15-30 mg equivalents per 100 g of the amine-modified epoxy resin, and the equivalent ratio of the organic acid to the metal salt is (0.3/1)-(5/1).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]Especially this invention relates to the cationic electrodeposition paint constituent which is excellent in throwing power of electrolytic colouring, gas pin-proof nature, HAJIKI-proof nature, etc. about a cationic electrodeposition paint constituent.

[0002]

[Description of the Prior Art]In order to protect a metallic material from corrosion and to maintain the aesthetic sense among duration of service, generally paint is performed to the surface. Since it can paint even into details and can paint automatically and continuously even if it is a coated object which has complicated shape, cathodic electrodeposition coating has shape large-sized [a car body etc.] and complicated, and is used widely as an under coat coating method of the coated object in which high rust prevention is demanded. As compared with other coating methods, it is economical from the utilization ratio of a paint being very high, and has spread widely as an industrial coating method.

[0003]Cathodic electrodeposition coating makes a coated object immersed as the negative pole into a cationic electrodeposition paint constituent, and is performed by impressing voltage. Since a deposit of the tunic in the process of this paint is based on an electrochemical reaction and the tunic which deposited on the coated object surface has insulation by impression of voltage, In a paint process, the electrical resistance of a tunic becomes large in proportion to the increase in thickness according to a deposit of a tunic advancing and the thickness of a deposit film increasing.

[0004]As a result, a deposit of the paint to the part concerned falls and a deposit of the tunic to an undeposited part starts instead. Thus, a paint emulsion particle covers an uncovered portion one by one, and paint is completed. It is called throwing power of electrolytic colouring among this Description that a tunic is formed in the uncovered part of a coated object one by one.

[0005]Such cathodic electrodeposition coating is usually used for under coat paint, and even if it is a coated object which has a complicated structure from performing rust prevention etc. as a key objective, it needs to carry out thickness of the tunic in all the portions beyond a predetermined value. In cathodic electrodeposition coating, since the insulating tunic is formed in the coated object surface one by one as mentioned above, it has infinite throwing power of electrolytic colouring theoretically, and the tunic should be able to be uniformly formed in all the portions of a coated object.

[0006]However, in the conventional cationic electrodeposition paint constituent, throwing power of electrolytic

colouring may not necessarily be enough, and the nonuniformity of thickness may produce it.

[0007]It is possible to lower the electric resistance value of a tunic into the tunic made to form, as a factor of a throwing-power-of-electrolytic-colouring fall, when an ionic group, hydration functional groups, etc. which are contained in the paint remain and these serve as a charge transfer medium. Therefore, in cathodic electrodeposition coating, in order to realize high throwing power of electrolytic colouring, it is necessary to remove such a factor.

[0008]On the other hand, the cationic electrodeposition paint constituent needs to show storage stability sufficient as distemper. Therefore, the ingredient of a cationic electrodeposition paint constituent of dispersion stability being shown in an aquosity medium and containing the ion more than a constant rate is inescapable.

[0009]That is, what is necessary is to lower the content of an ionicity ingredient and just to raise the electric resistance value of electrodeposition coating, in order to improve the throwing power of electrolytic colouring of a cationic electrodeposition paint constituent. However, the dispersion stability over the aquosity medium of a cationic electrodeposition paint constituent falls, and it becomes difficult to use it only by lowering the content of an ionicity ingredient as distemper.

[0010]In cathodic electrodeposition coating, water is electrolyzed in the surface of the coated object in which voltage is impressed as the negative pole, and hydrogen gas is emitted. A pinhole will be formed in a coat, if hydrogen gas is emitted simultaneously with a deposit of a tunic and the emitted hydrogen gas sparks. Such a pinhole is called the "gas pin" to the person skilled in the art. As for a gas pin, it is preferred to control, since it becomes a cause of a coating film defect.

[0011]There are some which are called "HAJIKI" to a person skilled in the art in the defect of an electrodeposition coat. It is known that the oil adhering to a paint film, etc. will bump and produce the defect of this kind of coat from the organic compound and the exterior of the low molecular weight contained in a coating composition at a subsequent heat cure process, for example. That is, since the tunic of the electrodeposited paint is fused and is in a flow state, a hole is easily vacant in a heat cure process, as for it with the local shock by bumping. Then, when a binder component hardens before surrounding resin carried out flattening and the hole was buried thoroughly, the hole of a paint film is fixed and the defect of a coat in which shape resembled the crater is formed.

[0012]Therefore, if scattering of the oil in the impurity and electrodeposition coating process in a coating composition, etc. are eliminated, such HAJIKI will not be produced, but especially when carrying out on a scale of industrial, it is difficult [it] to put it into practice. It is easy to produce HAJIKI especially with the coating composition of the hypoviscosity which is excellent in mobility.

[0013]In WO 98/No. 03701 gazette, improving the throwing power of electrolytic colouring of a cationic electrodeposition paint constituent is indicated by introducing triple bonds, such as an ethynyl group and a nitrile group, into base resin. Improving the throwing power of electrolytic colouring of a cationic electrodeposition paint constituent is indicated by by introducing a sulfonium group, a propargyl group, and a double bond into base resin at JP,2000-38525,A.

[0014]In JP,H11-182795,A, improving the gas pin-proof nature and throwing power of electrolytic colouring of a cationic electrodeposition paint constituent is indicated by using the 1st class amino group content resin, the 3rd class, and/or the 4th class onium salt group content resin as resin for pigment dispersion. In JP,H10-182795,A, improving the HAJIKI-proof nature of an electrodeposition coating composition is indicated by

adding the resultant of imidazoline group content polyoxyalkylene diamine and a polyphenol system epoxy resin.

[0015]Thus, improving each performance individually is shown by the above-mentioned advanced technology. However, since such performances are related mutually, it is difficult to improve all simultaneously.

[0016]

[Problem(s) to be Solved by the Invention]The dispersion stability over an aqueous medium has a place which this invention solves all the above-mentioned conventional problems simultaneously, and is made into the purpose in providing the cationic electrodeposition paint constituent which improved throwing power of electrolytic colouring, gas pin-proof nature, HAZI-proof nature, etc. without making it fall.

[0017]

[Means for Solving the Problem]This invention a binder component containing amine modified epoxy resin and a blocked polyisocyanate hardening agent, In a cationic electrodeposition paint constituent containing an emulsion which makes it distribute in an aqueous medium which contains metal salt of organic acid and organic acid as a neutralizer, and changes, A total amount of organic acid contained as the above-mentioned neutralizer is 15 - 30 milliequivalent to the amine modified epoxy resin 100g, equivalent ratio with metal salt of organic acid and organic acid provides a cationic electrodeposition paint constituent which are 0.3 / 1 - 5/1, and the above-mentioned purpose is attained by that.

[0018]

[Embodiment of the Invention]The binder component of a binder component electrodeposition coating composition is a thermosetting resin composition containing cation-ized resin and a hardening agent.

[0019]Cation-ized resin needs to be aqueous resin in which water dispersibility is shown. An amine-modified-epoxy-resin, amine denaturation polyurethane polyol resin, amine denaturation polybutadiene-resin, amine-modified-acrylic-resin, or sulfonium group content resin system, a phosphonium group content resin system, etc. are included in cation-ized resin, for example. Desirable cation-ized resin is amine modified epoxy resin.

[0020]Typically, amine modified epoxy resin carries out ring breakage of all of the epoxy groups of an epoxy resin by amine, or carries out ring breakage of some epoxy groups with other active hydrogen compounds, carries out ring breakage of the remaining epoxy groups by amine, and is manufactured.

[0021]an epoxy resin -- general -- the molecular weights 600-4000 -- desirable -- the 700 to 3000 weight per epoxy equivalents 300-2000 -- the thing of 350-1500 is used preferably. Typically, it is a polyphenol poly glycidyl ether type epoxy resin like bisphenol A, the bisphenol F, the bisphenol S, phenol novolac, and cresolnovolac.

[0022]An oxazolidone ring content epoxy resin like a description may be used for the formula of the 0004th paragraph of JP,H5-306327,A, and ** 3 as an epoxy resin. It is because the coat excellent in heat resistance and corrosion resistance is obtained.

[0023]It is obtained by carrying out heating heat insulation of the polyepoxide to the blocked polyisocyanate blocked with lower alcohol like methanol, for example under existence of a basic catalyst as a method of introducing an oxazolidone ring into an epoxy resin, and distilling out of the inside of a system the lower alcohol which carries out a byproduction.

[0024]Especially a desirable epoxy resin is an oxazolidone ring content epoxy resin given in Tokuganhei10-305294. It is because the coat which was excellent in heat resistance and corrosion resistance, and also was

excellent also in shock resistance is obtained. The example and manufacturing method of this oxazolidone ring content epoxy resin are indicated in the 0012-0047th paragraphs of Tokuganhei10-305294.

[0025]These epoxy resins may denaturalize by polyester polyol, polyether polyol, and suitable resin like the alkylphenol of monofunctional nature. As an example of the resin used for this denaturation, polycaprolactone diol and an ethyleneoxide addition condensation thing are mentioned.

[0026]Chain extension of the epoxy resin can be carried out using a reaction with an epoxy group, diol, or dicarboxylic acid. For the example of diol, ethylene glycol, 1,2-propylene glycol, Alkylene diol;1,2-cyclohexanediol, such as 1,3-propanediol, 1,4-butanediol, and 1,6-hexanediol, Alicyclic diol, such as 1,4-cyclohexanediol; aromaticdiol, such as bisphenol A, the bisphenol F, resorcinol, and hydroquinone, etc. are mentioned. For the example of dicarboxylic acid, succinic acid, adipic acid, azelaic acid, dodecanedioic acid, Aromatic dicarboxylic acid, such as aliphatic dicarboxylic acid, such as long chain aliphatic dicarboxylic acid of dimer acid, $C_{18} - C_{20}$ and terminal carboxyl group denaturation Butadiene Acrylonitrile, or phthalic acid, isophthalic acid, and terephthalic acid, etc. are mentioned.

[0027]Generally the amine which uses an epoxy group for carrying out ring breakage is the 1st class amine, secondary amine, and tertiary amine. As the example, a butylamine, octylamine, diethylamine, Dibutyl amine, methylbutyl amine, monoethanolamine, diethanolamine, There is secondary amine which blocked the 1st class amine, such as N-methylethanol amine, a triethylamine hydrochloride, N,N-dimethylethanolamine acetate, ketimine of aminoethylethanolamine, and diketimine of diethylenetriamine. Amines may use together and use two or more things.

[0028]Since it is 2 Eq when making the 1st class amine react, Polymer Division quantification of ***** and the epoxy resin is carried out as a chain elongation agent of an epoxy resin. As for these amine made to react to an epoxy group, it is preferred to use it with the equivalent mostly with the epoxy group of an epoxy resin.

[0029]As for the number average molecular weight by GPC analysis of amine modified epoxy resin, 600-4000 are preferred. Film formability is insufficient in a number average molecular weight being less than 600, and if 4000 is exceeded, emulsification and aqueous-izing are difficult.

[0030]The amino group equivalent of amine modified epoxy resin is 60 - 80 milliequivalent still more preferably 55 to 80 milliequivalent preferably 50 to 80 milliequivalent to the total weight of 100 g of amine modified epoxy resin and a blocked polyisocyanate hardening agent. The dispersion stability in the inside of the aquosity medium of a binder component falls that this amino group equivalent is less than 50 milliequivalent, and if 100 milliequivalent is exceeded, it will become insufficient improving of the throwing power of electrolytic colouring of an electrodeposition coating composition.

[0031]The hardening agent refers to the ingredient which stiffens the tunic of an electrodeposition coating composition by constructing a bridge in cation-ized resin. A hardening agent may usually be used for an electrodeposition coating composition. Generally, melamine resin and blocked polyisocyanate are preferred and blocked polyisocyanate is especially preferred. Blocked polyisocyanate means the polyisocyanate from which the isocyanate group was protected by the blocking agent.

[0032]In the example of the polyisocyanate which can be used for preparation of blocked polyisocyanate. Trimethylene diisocyanate, tetramethylene di-isocyanate, Pen reservoir CHIRENJISO cyanate, hexamethylene di-isocyanate, 1,2-propylene diisocyanate, 1,2-butylene diisocyanate, 2,3-butylene diisocyanate, 1,3-butylene diisocyanate, Aliphatic compounds, such as ethylidene diisocyanate and

butylidene diisocyanate, 1,3-cyclopentane diisocyanate, 1,4-cyclohexane diisocyanate, Aliphatic series cyclic compounds, such as 1,2-cyclohexane diisocyanate and isophorone diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 4 and 4'-diphenyl diisocyanate, 1,5-naphthalene diisocyanate, Aromatic-compounds [, such as 1,4-naphthalene diisocyanate,], 4, and 4'-diphenylmethane diisocyanate, Aliphatic series-aromatic compounds, such as 2,4-, 2,6-toluene diisocyanate or those mixture 4,4'-toluidine diisocyanate, 1, and 4-xylenediisocyanate, There are nuclear substitution aromatic compounds, such as dianisidine diisocyanate, 4, and 4-diphenyl ether diisocyanate and chlorodiphenyl diisocyanate, etc. 2,5- or 2,6-bis(isocyanate methyl)bicyclo[2.2.1] heptane (NBDI), a 1,3-diisocyanate methylcyclohexane (hydrogenation XDI), 4,4'-methylenebis (cyclohexylisocyanate) (hydrogenation MDI), etc. are mentioned.

[0033]The blocking agent used for preparation of blocked polyisocyanate means the low molecular weight compound made to react to the isocyanate group in an isocyanate temporarily, in order to prevent an isocyanate from reacting by room temperature environment. Generally, a blocking agent is desorbed from the bottom isocyanate group of heating.

[0034]The blocking agent can use what is known well in this field. For example, phenol system blocking agents, such as phenol, cresol, a xylenol, chlorophenol, and ethylphenol; Epsilon caprolactam, Active methylene system blocking agents, such as lactam system blocking agent; ethyl acetoacetate, acetylacetones, etc., such as delta-PARERO lactam, gamma-butyrolactam, and beta-PUROPIO lactam; Methanol, Ethanol, propanol, butanol, amyl alcohol, ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, Diethylene glycol monomethyl ether, propylene glycol monomethyl ether, Benzyl alcohol, glycolic acid methyl, glycolic acid butyl, diacetone alcohol, Alcohol system blocking agents, such as methyl lactate and ethyl lactate; Formaldoxime, Oxime system blocking agents, such as aceto aldoxime, acetoxime, methylethyl ketoxime, diacetylmonoxime, and cyclohexane oxime; Butyl mercaptan, hexyl mercaptan, t-butyl mercaptan, a thiophenol, methylthio phenol, Mercaptan system blocking agents, such as an ethylthiophenol; The acetic amide, acid-amide system blocking agent [, such as benzamide,]; -- imide system blocking agent [, such as succinimid and maleic acidimide,]; -- imidazole series blocking agent; pyrazole system blocking agent [, such as imidazole and 2-ethylimidazole];, a triazole series blocking agent, etc. can be mentioned. Among these, when it desires cold cure (160 ** or less), it is good to use a lactam system and an oxime system blocking agent.

[0035]In order to adjust the hardenability of a binder component, the cationic electrodeposition paint constituent of this invention may be made to contain a tin compound like dibutyltin dilaurate and Djibouti rutin oxide, and the usual urethane cleavage catalyst if needed. As for the quantity, it is preferred to use 0.1 to 5% of the weight of blocked polyisocyanate.

[0036]It combines with the cationic group contained in cation-ized resin, and a neutralizer neutralizer forms a salt, and refers to the ingredient which enables distribution of cation-ized resin to an aquosity medium. Generally, neutralizers are organic acid and inorganic acid. Generally electric dissociation exponents of a neutralizer are 0.9-4.8.

[0037]It uses more preferably combining metal salt of organic acid and organic acid as a neutralizer. It is because the cure rate of a binder component increases and the HAJIKI-proof nature of a coating composition is improved by using metal salt of organic acid.

[0038]Lactic acid, acetic acid, formic acid, sulfamic acid, etc. are mentioned as the example of desirable organic acid. Especially desirable organic acid is lactic acid.

[0039]Copper, nickel, cobalt, zinc, etc. are mentioned as the desirable example of organic acid and the metal which forms a salt. Especially desirable metal is zinc.

[0040]The cationic electrodeposition paint constituent of cationic electrodeposition paint constituent this invention is prepared by distributing the ingredient which other cationic electrodeposition paint constituents, such as above-mentioned amine modified epoxy resin and a hardening agent, are made to usually contain in the aqueous medium containing a neutralizer. What is necessary is just to perform distribution of an ingredient by the usual method.

[0041]Into an aqueous medium, various organic solvents may be used besides water for adjustment of the dissolution of resin, viscosity, etc. As an example of the solvent which can be used, hydrocarbon (for example, xylene or toluene). alcohols (for example, methyl alcohol and n-butyl alcohol.) Isopropyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, propylene glycol and ether (for example, ethylene glycol monoethyl ether.) Ethylene glycol monobutyl ether, ethylene glycol monohexyl ether, Propylene glycol monoethyl ether, 3-methyl-3-methoxybutanol, Diethylene glycol monoethyl ether, diethylene-glycol monobutyl ether, Those mixtures are mentioned after ketone (for example, methyl isobutyl ketone, cyclohexanone, isophorone, an acetylacetone) and ester species (for example, ethylene glycol monoethyl ether acetate, ethylene-glycol-monobutyl-ether acetate). The amount of these solvents used is 0.05 to 15 % of the weight preferably about 0.01 to 25% of the weight to the whole paint.

[0042]The quantity of a hardening agent is adjusted so that a good cured film may be given in response to the time of hardening with active hydrogen content functional groups, such as the 1st class, the 2nd class or/and the 3rd class amino group in cation-ized resin, and a hydroxyl group. expressing with the solid content weight ratio of amine modified epoxy resin and a hardening agent -- general -- 90 / 10 - 50/50 -- it is the range of 80 / 20 - 65/35 preferably.

[0043]The total amount of the organic acid contained as a neutralizer in an electrodeposition coating composition makes quantity of a neutralizer preferably the quantity which turns into 18 - 26 milliequivalent still more preferably 16 to 28 milliequivalent 15 to 30 milliequivalent to the amine modified epoxy resin 100g. The total amount of organic acid means the sum total of the quantity of the organic acid of isolation, and the quantity of the metal-salt-ized organic acid.

[0044]The emulsion stability in the inside of the aqueous medium of a binder component falls that the total amount of organic acid is less than 15 milliequivalent to the amine modified epoxy resin 100g, and if 30 milliequivalent is exceeded, the throwing power of electrolytic colouring of an electrodeposition coating composition will fall.

[0045]the content ratio with metal salt of organic acid and organic acid -- equivalent ratio -- 0.3 / 1 - 5/1 -- desirable -- 0.4 / 1 - 4/1 -- it is 0.5 / 1 - 4/1 more preferably.

[0046]The emulsion stability in the inside of the aqueous medium of a binder component falls that a content ratio with metal salt of organic acid and organic acid is less than 0.3/1 in equivalent ratio, if 5/1 is exceeded, the introduction amount of metal salt will decrease and the HAJIKI-proof nature of an electrodeposition coating composition will fall.

[0047]normal use of the ingredient which a cationic electrodeposition paint constituent other than the above-mentioned ingredient is made to usually contain if needed is carried out to the cationic electrodeposition paint constituent of this invention -- quantity addition can be carried out. As this ingredient, paints, pigment dispersion resin, a viscosity modifier, a surface-active agent, an antioxidant, an ultraviolet ray absorbent, etc.

can be mentioned, for example.

[0048]A cationic electrodeposition paint constituent is made to contain paints in order to give color, concealment, and corrosion resistance to a coat generally. The paints usually used also for the electrodeposition coating composition of this invention may be made to contain. A color pigment like a titanium white, carbon black, and red ocher as an example of these paints, Kaolin, talc, aluminum silicate, calcium carbonate, mica, Clay and an extender like silica, zinc phosphate, iron phosphate, aluminium phosphate, A rust preventive pigment like calcium phosphate, phosphorous acid zinc, a zinc cyanide, a zinc oxide, Tripoli aluminium phosphate, molybdic acid zinc, molybdic acid aluminum, calcium molybdate, and aluminum molybdophosphate, etc. are mentioned.

[0049]When using paints as an ingredient of an electrodeposition coating composition, an aquosity medium is made to distribute paints at high concentration beforehand generally, and it is made paste state. It is because paints are powder state, so it is difficult to distribute the low concentration uniform state used with an electrodeposition coating composition at one process. Generally such a paste is called pigment dispersion paste.

[0050]With resin for pigment dispersion, it is made to distribute in an aquosity medium and a pigment dispersion paste prepares paints. Generally as pigment dispersion resin, cationic polymers, such as a modified epoxy resin which has a cationic or nonionic low-molecular-weight surface-active agent, and the 4th class ammonium and/or the 3rd class sulfonium group, are used. Generally, paints are used by 100 weight sections and an aquosity medium is used by the solid content ratio of ten to 100 weight section.

[0051]After mixing these ingredients, a mixture is distributed until paints serve as uniform predetermined particle diameter, and a pigment dispersion paste is obtained. A dispersion device is usually used for distribution. For example, a ball mill, a SANDOGU lined mill, etc. are used. The particle diameter of the paints included in a pigment dispersion paste is usually 15 micrometers or less.

[0052]As for the loadings of a pigment dispersion paste, when blending a pigment dispersion paste with a cationic electrodeposition paint constituent, it is preferred among a cationic electrodeposition paint constituent that paints consider it as the quantity which does not exceed 50 % of the weight as solid content.

[0053]When performing electropainting using the cationic electrodeposition paint constituent of electropainting this invention, what was not limited especially when there was conductivity as a coated object, for example, carried out the surface treatment of a griddle, a steel plate, an aluminum plate, and these, such molding, etc. can be mentioned.

[0054]By using a coated object as the negative pole, electropainting impresses the voltage of 50-450V between the anodes, and is usually performed. If it becomes being less than [50V] electrodepositing impressed electromotive force insufficient and it exceeds 450V, power consumption becomes large and is uneconomical. A uniform tunic can be formed in the whole coated object, without producing the rapid rise of thickness in an electrodeposited process, if voltage is impressed within the limits of above-mentioned using the constituent of this invention.

[0055]As for the bath liquid temperature of the cationic electrodeposition paint constituent in the case of impressing the above-mentioned voltage, 10-45 °C is usually preferred.

[0056]As for an electrodeposited process, it is preferred the process in which carry out the negative pole of the process in which a coated object is immersed in a (i) cationic electrodeposition paint constituent, and the (ii) above-mentioned coated object, impress voltage between the anodes, and a tunic is deposited, and to be

** constituted. Although time to impress voltage changes with electrodeposited conditions, generally it can be made into 2 to 4 minutes.

[0057]After the end of an electrodeposited process, and after remaining as it is or rinsing, preferably, the electrodeposition coating produced by making it above is 160-220 **, is stiffened by printing for 10 to 30 minutes, and completes 120-260 ** of paint.

[0058]As for the thickness of the electrodeposition coat after hardening, when the cationic electrodeposition paint constituent of this invention is used, 10-25 micrometers is preferred. Rust prevention is insufficient in it being less than 10 micrometers, and if it exceeds 25 micrometers, it will lead to waste of a paint.

[0059]Thus, according to the purpose, as for the coated object in which the coat obtained was formed, a required second coat and/or finishing are given further. For example, the solvent type for generally giving chipping-proof nature in the case of the shell for cars, The two quart 1 bake coating method which applies a base coating and applies a clear coating material further without stiffening this after applying and printing the intermediate coat of aquosity or a granular material and which is painted by what is called the wet one wet method, and prints the coat of these simultaneously after that is applied.

[0060]

[Example]Although the following working example explains this invention still more concretely, this invention is not limited to these. Among working example, a "part" and "%", unless it refuses, it is based on a weight reference.

[0061]The synthetic agitator of example of manufacture 1 amine modified epoxy resin, a condenser tube, a nitrogen introducing pipe, 92 copies of 2,4- / 2,6-tolylene diisocyanate (weight ratio = 8/2), 95 copies of methyl isobutyl ketone (MIBK), and 0.5 copy of dibutyltin dilaurate were taught to the flask equipped with a thermometer and a tap funnel. 21 copies of methanol was dropped under churning of a reaction mixture. The reaction was begun from the room temperature and temperature up was carried out to 60 ** by generation of heat. Then, after continuing a reaction for 30 minutes, 57 copies of ethylene glycol mono-2-ethylhexyl ether was dropped from the tap funnel. 42 copies of 5 mol of bisphenol A-propylene oxide adducts were added to the reaction mixture. The reaction was mainly performed in 60-65 **, and in measurement of an IR spectrum, it continued until the absorption based on an isocyanate group disappeared.

[0062]Next, 365 copies of epoxy resins of the weight per epoxy equivalent 188 compounded by the known method from bisphenol A and epichlorohydrin were added to the reaction mixture, and temperature up was carried out to 125 **. Then, 1.0 copy of benzyldimethylamine is added, and it was made to react at 130 ** until it became 410 copies of weight per epoxy equivalents.

[0063]Then, when 87 copies of bisphenol A was added and it was made to react at 120 **, the weight per epoxy equivalent was set to 1190. Then, the reaction mixture was cooled, 25 copies of 79-% of the weight MIBK solutions of the ketimine ghost of 11 copies of diethanolamines, 24 copies of N-ethyl ethanolamines, and aminoethylethanolamine were added, and it was made to react at 110 ** for 2 hours. Then, it diluted until it became 80% of a nonvolatile matter by MIBK, and amine modified epoxy resin (80% of resin solid content) was obtained.

[0064]The amino group equivalent of this amine modified epoxy resin was 86 meq(s)/100g.

[0065]1250 copies of synthetic 4,4'-diphenylmethane diisocyanate and 266.4 copies of methyl isobutyl ketone of example of manufacture 2 hardening agent were taught to the reaction vessel, these were heated until it became 80 **, and 2.5 copies of dibutyltin dilaurate was added. The solution in which 944 copies of

butyls cellosolve (ethylene glycol monobutyl ether) were made to dissolve 226 copies of epsilon caprolactam was dropped at the above-mentioned reaction vessel over 2 hours at 80 **. It checked that raised temperature to 100 **, heated for 4 hours, and the absorption spectrum of the isocyanate group had disappeared. Subsequently, 336.1 copies of methyl isobutyl ketone was added, and the blocked polyisocyanate hardening agent was obtained.

[0066]222 copies of synthetic isophorone diisocyanate (IPDI) of example of manufacture 3 hardening agent (half block isocyanate) is put into a reaction vessel, After diluting with 39.1 copies of methyl isobutyl ketone, 0.2 copy of dibutyltin dilaurate was added, temperature up was carried out to 50 **, and 131.5 copies of 2-ethylhexanol was added over 2 hours so that resin temperature might not exceed 55 **. Reaction temperature was maintained at 50 ** for 1 hour, agitating, and the half block isocyanate curing agent was obtained.

[0067]Bisphenol A type epoxy resin (made by Dow Chemical company company) 382.2 weight section of the weight per epoxy equivalent 188 and bisphenol A 117.8 weight section are taught to the preparation reaction vessels of example of manufacture 4 pigment-dispersion resin, The bottom of a nitrogen atmosphere, and after making it react at 150-160 ** for 1 hour and cooling at 120 **, 2-ethylhexanol half block IPDI(MIBK solution)209.8 weight section prepared in the example 3 of manufacture was added. After making it react at 140-150 ** for 1 hour, ethylene-glycol-monobutyl-ether 205.0 weight section was added, and it cooled at 60-65 **.

[0068]There 1-(2-hydroxyethyl thio)-2-propanol 408.0 weight section, Deionized water 144.0 weight section and dimethylol-propionic-acid 134 weight section are added, The 3rd class sulfonium base content epoxy resin for pigment dispersion was obtained by making it react at 65-75 ** until acid value is set to 1, introducing the 3rd class sulfonium group into an epoxy resin, adding the amount part of deionized water 1595. duplexs, and terminating the 3rd class-ization (30% of resin solid content).

[0069]200 copies of pigment dispersion resin obtained in the example 4 of manufacture to the preparation SANDOGU lined mill of the example of manufacture 5 pigment-dispersion paste, 18.0 copies of 2.0 copies of carbon black, 100.0 copies of kaolin, 80.0 copies of titanium dioxide, and aluminum molybdophosphate and ion exchange water were put in, it distributed until it became a particle size of 10 micrometers or less, and the lead free pigment dispersion paste was obtained (60% of solid content).

[0070]The hardening agent of the example 2 of manufacture was uniformly mixed with amine denaturation epoxy nature resin of the example 1 of preparation manufacture of a working example 1 cationic-electrodeposition-paint constituent with the solid content compounding ratio 70:30. At this time, the amine equivalent was 60meq to the total weight of 100 g of amine modified epoxy resin and a blocked polyisocyanate hardening agent.

[0071]Then, ethylene glycol mono-2-ethylhexyl ether was added so that it might become 3% to solid content. 8.0 copies of lactic acid (electric dissociation exponent is 3.862) was added 50% to 800 copies of this binder component, and 12.0 copies of lactic acid zinc was added. The total amount of organic acid is 20 milliequivalent to the total weight of 100 g of amine modified epoxy resin and a blocked polyisocyanate hardening agent. Ion exchange water was added and it diluted slowly. It was considered as the main emulsion by removing MIBK under decompression so that solid content might be 36.0%.

[0072]420.2 copies of pigment dispersion pastes obtained in 1580.2 copies of this main emulsion and the example 5 of manufacture were mixed with 2025.2 copies of ion exchange water, and 9.3 copies of Djibouti

rutin oxide, and the cationic electrodeposition paint of 20.0 % of the weight of solid content was prepared. The solid content weight ratio of the pigment content in an electrodeposition paint and a total resin content was 1/3.5.

[0073]The throwing power of electrolytic colouring of the cationic electrodeposition paint constituent prepared in this way, gas pin-proof nature, HAJIKI-proof nature, and storage stability were evaluated. The evaluation result was shown in Table 4.

[0074]The cationic electrodeposition paint constituent obtained by evaluation procedure (A) throwing-power-of-electrolytic-colouring working example was used, and four-sheet box throwing power of electrolytic colouring was measured with the measuring device shown in drawing 1. 4 l. of prepared electrodeposition paints were paid to the electropainting container (100x250x200 mm) of plastic character, and it agitated with the magnetic stirrer. The zinc phosphate treated steel sheet (surfboard dyne SD-5000 processing of JIS G3141 SPCC-SD) of four sheets is used, The interval of the steel plate was 20 mm each, the hole of 8 mmphi was vacated by the 3rd sheet from the counter electrode, and the evaluation plate of the case shape structure which enabled it to invade a paint only from the above-mentioned hole was produced, and it installed into the above-mentioned electropainting container so that the distance to a counter electrode might be set to 150 mm.

[0075]The flank of the evaluation plate of the above-mentioned case shape structure performs electric insulating treatment, and was kept from making a coat form in this flank. Voltage was impressed and painted between counter electrodes by using the above-mentioned evaluation plate as the negative pole.

[0076]Pressure up of the paint was carried out to predetermined voltage in 5 seconds after an impression start, and it was performed by maintaining Sadamu Madokoro's voltage for 175 seconds after that. The bath temperature at this time was adjusted at 30 **. After rinsing the evaluation plate after paint, it was burned for 20 minutes at 170 **, measured the thickness of the evaluation plate A nearest to a counter electrode, and the thickness of G side of the furthest evaluation plate from a counter electrode after air cooling, and asked for the film parameter (G/A value (%)) of G side and A side.

[0077](B) The cold rolled sheet steel (size: 70x150 mm) which carried out zinc phosphate processing was dipped in the electro-deposition bath containing a gas pin-proof nature cationic electrodeposition paint constituent. Voltage was impressed to this steel plate, it applied for 5 seconds, pressure up was carried out to the voltage of 200V, and it was electrodeposited for 175 seconds. Then, it rinsed, it printed for 10 minutes at 160 **, and the cathodic electrodeposition coat was obtained. Subsequently, using the cold rolled sheet steel of four sheets, voltage was changed to 220V, 240V, 200V, and 280V, respectively, and this operation was repeated.

[0078]Visual observation of the painted-surface state of the obtained coat was carried out, and the existence of the gas pin estimated on the following standards.

[0079]Valuation basis : [Table 1]

5	280V以上でガスピン無し
4	240V以上でガスピン無し
3	220V以上でガスピン無し
2	200V以上でガスピン無し
1	200Vでガスピン有り

[0080](C) The HAJIKI-proof nature cationic electrodeposition paint constituent was electrodeposited so that it might become the cold rolled sheet steel (size: 10 cm x 15 cm) which carried out zinc phosphate processing with 20 micrometers of dry membrane thickness. This electropainting board was rinsed and room temperature neglect was carried out for 10 minutes.

[0081]The painted surface was turned upward, the electropainting board was placed horizontally, and the cup made from aluminum foil 15 mm in diameter and 5 mm in height was stuck in the center of a board with the double-sided tape. It put slushing oil and one drop of water at a time into this cup made from aluminum foil by the syringe.

[0082]The coated plate which attached the cup was maintained horizontally in the oven set as 160 **, and it was able to be printed for 10 minutes. Visual evaluation of the coating film defect of the shape of a crater which the oil dispersed and generated on the electrodeposition coat surface on the wet board after baking was carried out by the following valuation bases.

[0083]Valuation basis : [Table 2]

5	塗膜表面にクレーター等の異常がなく、平滑である
4	塗膜表面に直径2mm以下で浅いクレーターがわずかに発生する
3	塗膜表面に直径3mm以下で浅いクレーターが発生する
2	塗膜表面に直径3mmより大きく、浅いクレーターが発生する
1	塗膜表面に直径3mmより大きく、深いクレーターが多数発生する

[0084](D) 2 l. of storage stability electrodeposition paints were stored for two weeks at 40 ** under churning. This paint was filtered at the wire gauze of 380 meshes, and residue was measured (1 kg of mg / paints). The following valuation bases estimated storage stability from the amount of residue.

[0085]Valuation basis : [Table 3]

○	50mg／塗料1kg未満
△	50mg／塗料1kg以上100mg／塗料1kg未満
×	100mg／塗料1kg以上

[0086]The cationic electrodeposition paint constituent was obtained like working example 1 except using the hardening agent of the example 3 of manufacture instead of the hardening agent of the example 2 of preparation manufacture of a working example 2 cationic-electrodeposition-paint constituent. The throwing power of electrolytic colouring of the obtained cationic electrodeposition paint constituent, gas pin-proof nature, HAJIKI-proof nature, and storage stability were evaluated like working example 1. The evaluation result was shown in Table 4.

[0087]The addition of 50% of preparation lactic acid of a working example 3 cationic-electrodeposition-paint constituent was made into 17.0 copies, and the cationic electrodeposition paint constituent was obtained like working example 1 except making the addition of lactic acid zinc into 12.0 copies (equivalent ratio with metal salt of organic acid and organic acid: 1.2/1). The throwing power of electrolytic colouring of the obtained cationic electrodeposition paint constituent, gas pin-proof nature, HAJIKI-proof nature, and storage stability were evaluated like working example 1. The evaluation result was shown in Table 4.

[0088]The synthetic agitator of example of comparison manufacture 1 amine modified epoxy resin, a condenser tube, a nitrogen introducing pipe, 92 copies of 2,4- / 2,6-tolylene diisocyanate (weight ratio = 8/2),

95 copies of methyl isobutyl ketone (MIBK), and 0.5 copy of dibutyltin dilaurate were taught to the flask equipped with a thermometer and a tap funnel. 21 copies of methanol was dropped under churning of a reaction mixture. The reaction was begun from the room temperature and temperature up was carried out to 60 ** by generation of heat. Then, after continuing a reaction for 30 minutes, 57 copies of ethylene glycol mono-2-ethylhexyl ether was dropped from the tap funnel. 42 copies of 5 mol of bisphenol A-propylene oxide adducts were added to the reaction mixture. The reaction was mainly performed in 60-65 **, and in measurement of an IR spectrum, it continued until the absorption based on an isocyanate group disappeared.

[0089]Next, 365 copies of epoxy resins of the weight per epoxy equivalent 188 compounded by the known method from bisphenol A and epichlorohydrin were added to the reaction mixture, and temperature up was carried out to 125 **. Then, 1.0 copy of benzyldimethylamine is added, and it was made to react at 130 ** until it became 410 copies of weight per epoxy equivalents.

[0090]Then, 54 copies of bisphenol A was added and it was made to react at 120 **. Then, the reaction mixture was cooled, 35 copies of 79-% of the weight MIBK solutions of the ketimine ghost of 15.4 copies of diethanolamines, 33.6 copies of N-ethyl ethanolamines, and aminoethylethanolamine were added, and it was made to react at 110 ** for 2 hours. Then, it diluted until it became 80% of a nonvolatile matter by MIBK, and amine modified epoxy resin (80% of resin solid content) was obtained. The amino group equivalent of this amine modified epoxy resin was 130 meq(s)/100g.

[0091]Amine modified epoxy resin of the example 1 of comparison manufacture is used instead of amine modified epoxy resin of the example 1 of preparation manufacture of a comparative example 1 cationic-electrodeposition-paint constituent, The addition of lactic acid was made into 24.9 copies 50%, and the cationic electrodeposition paint constituent was obtained like working example 1 except making the addition of lactic acid zinc into 12.0 copies (organic-acid total amount: 35 meq/100 g, and equivalent ratio:1/1.7 with metal salt of organic acid and organic acid). The throwing power of electrolytic colouring of the obtained cationic electrodeposition paint constituent, gas pin-proof nature, HAJIKI-proof nature, and storage stability were evaluated like working example 1. The evaluation result was shown in Table 4.

[0092]The addition of 50% of preparation lactic acid of a comparative example 2 cationic-electrodeposition-paint constituent was made into 22.5 copies, and the cationic electrodeposition paint constituent was obtained like working example 1 except not adding lactic acid zinc. The throwing power of electrolytic colouring of the obtained cationic electrodeposition paint constituent, gas pin-proof nature, HAJIKI-proof nature, and storage stability were evaluated like working example 1. The evaluation result was shown in Table 4.

[0093]

[Table 4]

実施例 No.	1	2	3	比較 1	比較 2
有機酸総量	20	20	28	35	20
有機酸／金属塩 当量比	0.6/1	0.6/1	1.2/1	1.7/1	1/0
つきまわり性	0.57	0.5	0.47	0.30	0.46
耐ガスピン性	5	4	4	2	4
耐ハジキ性	4	4	4	3	1
貯蔵安定性	○	○	○	○	○

[0094]From this result, the cationic electrodeposition paint constituent obtained by working example was

improving notably compared with the conventional cationic electrodeposition paint constituent about throwing power of electrolytic colouring, gas pin-proof nature, and HAJIKI-proof nature, and it was shown that storage stability is equivalent to the conventional cationic electrodeposition paint constituent.

[0095]

[Effect of the Invention]The cationic electrodeposition paint constituent which improved throwing power of electrolytic colouring, gas pin-proof nature, HAJIKI-proof nature, etc. was provided without reducing the dispersion stability over an aquosity medium.

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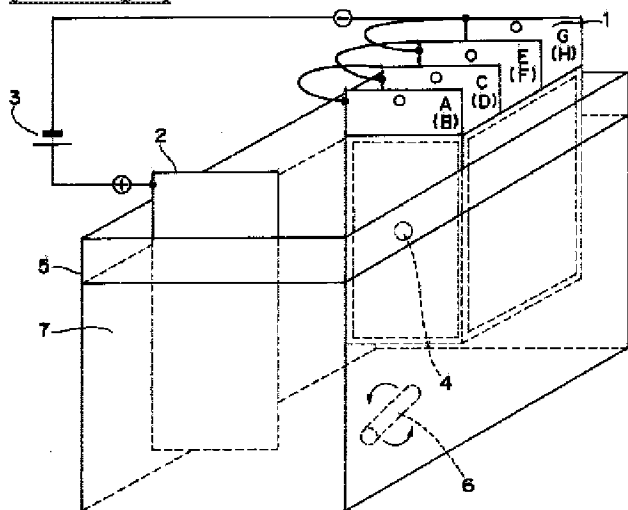
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DRAWINGS

[Drawing 1]



[Translation done.]